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(54) **Water-resistant protective overcoat for AGX photographic systems**

(57) The present invention is an imaged photographic element having a protective overcoat thereon. The protective overcoat formed by the steps of providing a photographic element having at least one silver halide light-sensitive emulsion layer; applying a coating comprising hydrophobic polymer particles having an average size of 0.01 to 1 microns, a melting temperature of from 55 to 200 °C at a weight percent of 30 to 95, and gelatin at a weight percent of 5 to 70 over the at least one silver halide light-sensitive emulsion layer. The silver halide light sensitive emulsion layer is developed to provide an imaged photographic element. The hydrophobic polymer particles are then fused to form a protective overcoat. In an alternate embodiment the coating further includes water soluble polymer materials at a weight percent of from 5 to 45.

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to provide an imaged photographic element. The hydrophobic polymer particles are then fused to form a protective overcoat. In an alternate embodiment the coating further includes water soluble polymer materials at a weight percent of from 5 to 45.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides a novel overcoat formulation to the emulsion side of photographic products, particularly photographic prints, which encounters frequent handling and abuse by end users. The overcoat formulation of the present invention includes 30-95% by weight (based on the dry laydown of the overcoat) of hydrophobic polymer particles having an average size of 0.01-1 microns, preferably 0.01 to 0.5 microns and 5-70% by weight (based on the dry laydown of the overcoat) of gelatin as binder. Gelatin includes lime processed gelatin, acid processed gelatin and modified gelatin as described in U.S. Patent Nos. 5,219,992 and 5,316,902. Other common addenda, such as hardeners, spreading agents, charge control agents, dry scratch resistance compounds and lubricants can also be included in the formulation as needed. The hydrophobic polymer of this invention has melting temperature (T_m) of 55-200 °C, and forms a water-resistant layer by fusing the polymer particles at a temperature above the T_m after the sample has been processed to generate the image. Since the particle size of polymer is small, the overcoat layer will not adversely affect the sharpness of the image due to light scattering, as observed by other large particle fillers. The presence of 5-70% by weight of gelatin is sufficient to allow proper permeability for processing solution to diffuse in and out for image development and also retain particles in the layer during processing. The coating solution is aqueous and can be incorporated in the manufacturing coating operation without any equipment modification. The fusing step is simple and environmentally friendly to photofinishing laboratories. Polymer of choice can be any hydrophobic polymer or copolymer as long as the melting temperature is above 55 °C and below 200 °C. The lower limit is to prevent premature coalescence from occurring prior to photographic processing, and the upper limit is to prevent destruction of the paper support and imaging chemicals during fusing. These types of hydrophobic particles (polymers) include dispersion of submicron size, from 0.01 μm to 1 μm wax particles such as those offered commercially as aqueous or non-aqueous dispersions of polyolefins, polypropylene, polyethylene, high density polyethylene, oxidized polyethylene, ethylene acrylic acid copolymers, microcrystalline wax, paraffin, and natural waxes such as carnauba wax, and aqueous dispersions of synthetic waxes from such companies as, but not limited to, Chemical Corporation of America (Chemcor), Inc., Michelman Inc., Shamrock Technologies Inc., Daniel Products Company. The dispersion may also contain dispersing aids such as polyethylene glycol.

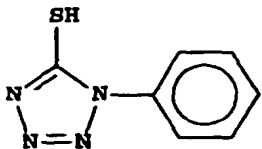
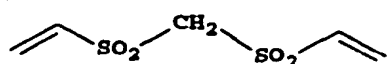
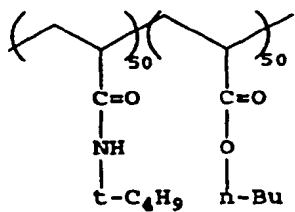
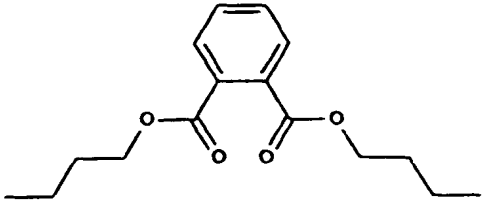
The imaged photographic elements protected in accordance with this invention are derived from silver halide photographic elements that can be black and white elements (for example, those which yield a silver image or those which yield a neutral tone image from a mixture of dye forming couplers), single color elements or multicolor elements. Multicolor elements typically contain dye image-forming units sensitive to each of the three primary regions of the spectrum. The imaged elements can be imaged elements which are viewed by transmission, such as negative film images, reversal film images and motion picture prints or they can be imaged elements that are viewed by reflection, such as paper prints. Because of the amount of handling that can occur with paper prints and motion picture prints, they are preferred imaged photographic elements for use in this invention.

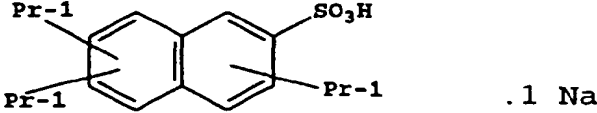
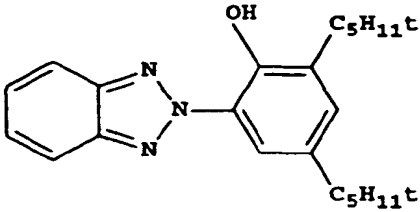
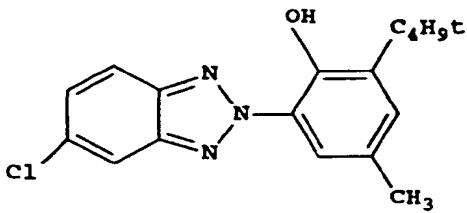
The photographic elements in which the images to be protected are formed can have the structures and components shown in Research Disclosure 37038. Specific photographic elements can be those shown on pages 96-98 of Research Disclosure 37038 as Color Paper Elements 1 and 2. A typical multicolor photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler, and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element can contain additional layers, such as filter layers, interlayers, overcoat layers, subbing layers, and the like. All of these can be coated on a support which can be transparent (for example, a film support) or reflective (for example, a paper support). Photographic elements protected in accordance with the present invention may also include a magnetic recording material as described in Research Disclosure, Item 34390, November 1992, or a transparent magnetic recording layer such as a layer containing magnetic particles on the underside of a transparent support as described in US 4,279,945 and US 4,302,523.

Suitable silver halide emulsions and their preparation, as well as methods of chemical and spectral sensitization, are described in Sections I through V of Research Disclosure 37038. Color materials and development modifiers are described in Sections V through XX of Research Disclosure 37038. Vehicles are described in Section II of Research Disclosure 37038, and various additives such as brighteners, antifoggants, stabilizers, light absorbing and scattering materials, hardeners, coating aids, plasticizers, lubricants and matting agents are described in Sections VI through X and XI through XIV of Research Disclosure 37038. Processing methods and agents are described in Sections XIX and XX of Research Disclosure 37038, and methods of exposure are described in Section XVI of Research Disclosure

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Layer	Laydown (mg/sq.ft.)
Overcoat	120.0 gelatin
	1.0 SURF-1
	0.39 SURF-2
	8.87 HAR-1
UV	12.11 UV-1
	2.13 UV-2
	3.57 SCV-1
	2.37 S-1
	2.37 S-2
	47.5 Gelatin
Cyan	18.1 Red light sensitive AgX
	39.31 C-1
	38.52 S-2
	3.22 S-3
	25.31 UV-1
	129.0 Gelatin
UV	17.43 UV-1
	3.07 UV-2
	5.14 SCV-1
	3.41 S-1
	3.41 S-2
	68.4 Gelatin
Magenta	7.70 Green-light sensitive AgX
	1.11 KCL
	29.5 C-2
	8.26 S-2
	3.54 S-4
	17.7 ST-1
	2.01 ST-2
	57.0 ST-3
	0.05 FOG-1
	0.285 Nitric Acid
	117.0 Gelatin

5 <u>FOG-1</u>	
10 <u>HAR-1</u>	
15 <u>P-1</u>	
20 <u>S-1</u>	1,4-Cyclohexylenedimethylene bis(2-ethylhexanoate)
25 <u>S-2</u>	
30 <u>S-3</u>	2-(2-Butoxyethoxy)ethyl acetate
35 <u>S-4</u>	Di-undecylphthalate

<u>SURF-1</u>	
<u>SURF-2</u>	$C_8F_{17}SO_3N(C_2H_5)_4$
<u>UV-1</u>	
<u>UV-2</u>	

Study of Dye density development by RA4 process

After the samples were fully hardened (at least 3 days after coating), they were exposed to 1/10 seconds of daylight of color temperature 3000K, through 0-3 density step chart in combination with a WR98 filter (blue light) and a heat absorbing filter. In the case of red light and green light, WR29 and WR99 filters were used respectively. After exposure, samples were processed with the Kodak RA4 process to generate color density. The assessment of developability was done by comparing the DlogE curves of each color record, particularly the yellow layer, to the check coating (sample No. 1 containing only gelatin in the overcoat). Lower dye density is the indicative of slow developability.

Test for Water Resistance

Ponceau Red dye is known to stain gelatin through ionic interaction, therefore it is used to test water resistance. Ponceau red dye solution was prepared by dissolving 1 gram dye in 1000 grams mixture of acetic acid and water (5 parts: 95 parts). Samples, without being exposed to light, were processed through the Kodak RA4 process to obtain white Dmin samples. These processed samples were then passed through a set of heated pressurized rollers (fusing) to convert the polymer particles of the overcoat into a water resistant layer. The water permeability was done by soaking fused samples in the dye solution for 5 minutes followed by a 30-second water rinse to removed excess dye solution on the coating surface. Each sample was then air dried, and status A reflectance density on the soaked area was recorded. Optical density of 3 indicates a completely water permeable coating, such as sample No. 1, its water resistance=0%. Relative to an optical density of 3 (sample No.1) being 0% water resistance and an optical density of 0 being 100% water resistant, the percent water resistance is calculated by the following equation.

$$\% \text{ water resistance} = 1 - (\text{status A density}/3)$$

Example 1

The polymer particles used to demonstrate this invention and their properties are listed below.

Table 1.

Sample ID	Overcoat Composition (in mg/sq.ft.)	Note	Yellow layer image developability
1	120 gel	comparison	98%
2	30 gel + 60 ME02925	invention	98%
3	30 gel + 90 ME02925	invention	98%
4	30 gel + 120 ME02925	invention	98%
5	40 gel + 60 ME02925	invention	100%
6	40 gel + 90 ME02925	invention	98%
7	40 gel + 120 ME02925	invention	97%
8	40 gel + 160 ME02925	invention	97%
9	50 gel + 60 ME02925	invention	99%
10	50 gel + 90 ME02925	invention	98%
11	50 gel + 120 ME02925	invention	97%
12	50 gel + 160 ME02925	invention	97%
13	40 gel + 60 ME39253	invention	99%
14	40 gel + 90 ME39253	invention	100%
15	40 gel + 120 ME39253	invention	99%
16	40 gel + 160 ME39253	invention	99%
17	40 gel + 60 PE392N35	invention	100%
18	40 gel + 90 PE392N35	invention	97%
19	40 gel + 120 PE392N35	invention	98%
20	40 gel + 160 PE392N35	invention	97%
C-1	60 gel + 60 Latex 1	comparison	100%
C-2	20 gel + 100 Latex 1	comparison	100%

For comparison, C-1 and C-2 were prepared. Latex 1 is a copolymer latex of approximately 80 nm average particle size, its composition is 95% of butylacrylate and 5% 2-sulfo-1,1-dimethylethyl acrylamide, sodium salt. This latex has a glass transition of -50°C and no melting temperature as it is not a crystalline polymer.

As shown in the table 1, the developability of image layers remained acceptable for samples containing as high as 80% hydrophobic particles in the overcoat.

Example 2

Samples as described in example 1 were processed by the Kodak RA4 process, dried, then passed through a set

Table 5

Sample ID	Overcoat Composition (in mg/sq.ft.)			Water Resistance		
	Gelatin	Polymer particle ME02925	Cyanamer N-10	fused @110C	fused @130C	fused @150C
4-1	120	0	0	0%	0%	0%
4-2	20	80	0	88%	90%	89%
4-3	20	80	20	94%	94%	89%
4-4	20	80	40	90%	65%	61%
4-5	30	70	0	92%	90%	84%
4-6	30	70	20	92%	90%	27%
4-7	30	70	40	90%	93%	84%
4-8	40	60	0	93%	94%	71%
4-9	40	60	20		93%	86%
4-11	40	160	0	93%	96%	93%
4-13	40	160	80	94%	96%	94%
4-14	60	140	0	25%	95%	93%
4-16	60	140	80	95%	95%	90%
4-17	80	120	0	16%	20%	18%
4-18	80	120	40	18%	24%	17%
4-19	80	120	80	94%	96%	92%

sitive emulsion layer;

developing the at least one silver halide light sensitive emulsion layer to provide an imaged photographic element; and

fusing the hydrophobic polymer particles to form a protective overcoat.

7. The imaged photographic element having the protective overcoat of claim 6 wherein the size of hydrophobic polymer particles is between 0.01 and 1.0 microns, more preferably between 0.01 to 0.5 microns.
8. The imaged photographic element having the protective overcoat of claim 6 wherein the water soluble polymer materials are selected from the group consisting of polyacrylamide, polymethacrylamide, poly(acrylic acid), poly(methacrylic acid), poly(ethylene oxide), poly(oxymethylene), poly(vinyl alcohol), polyvinylamine, polyvinylpyrrolidone, poly(vinyl pyridine), poly(ethyleneimine), poly(ethylene glycol methacrylate), poly(hydroxyethyl methacrylate), poly(vinyl methyl ether), poly(styrene sulfonic acid), poly(ethylene sulfonic acid), poly(vinyl phosphoric acid) and poly(maleic acid).
9. The imaged photographic element having the protective overcoat of claim 6 wherein the water soluble polymer materials have a molecular weight of from 1,000 to 200,000, preferably from 1,500 to 20,000.
10. The imaged photographic element having the protective overcoat of claim 6 wherein the hydrophobic polymer particles comprise a polymer selected from the group consisting of polyolefins, polypropylenes, polyethylenes, high density polyethylenes, oxidized polyethylenes, ethylene acrylic acid copolymers, microcrystalline waxes, paraffin, and natural waxes.